NASA Research Grant 01-007-001.

Annual Report -(1970-71)

Project:
" The Effect of Surface Conditions on the Work Function of Insulators and Semi-conductors."

Submitted by:
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To

The Office of University Affairs, Code Y,

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ANNUAL PROGRESS REPORT

NASA RESEARCH GRANT 01-007-001

Introduction

In continuance of the detailed annual report submitted in August 1970, the research work on the determination of ionization energies of a few organic semiconductors has progressed satisfactorily and reliable results have been obtained.

In the previous annual report, emphasis has been made on the following points:

1) The importance of ionization measurements of semiconductors in understanding their properties and structures in different ambient atmospheres.

2) A short up to date review of the work done, results obtained and theories evolved for adsorption of gases by metals and semiconductors.

3) The present experiment - the theory and the experimental technique

4) The experimental set up in determining the ionization energies in air atmosphere, the lay out consisting of

   a) the central chamber
   b) the optical unit
   c) power supply unit
   d) observation unit

5) The technique of measurement.

6) Outline of the intended programme of research.

The Progress of Work 1970-71

I. Determination of Ionization Energies in Air

With the experimental layout already set up, measurements of ionization energies were continued with a number of organic semiconductors in air atmosphere. The crystals used in the work were specially prepared and cent percent pure. The results are found to be in good agreement with the already existing values published for some of the crystals.

Results

Substance	Ionization Energy in Air
1. Anthracene	4.55 ev.
2. Magnesium Phthalocyanine	4.77 ev.
3. Graphite	4.65 "
4. Tetracene	4.80 "
5. Pentacene	4.60 "
6. Zinc Phthalocyanine	5.12 "
7. Copper Phthalocyanine	4.70 "
8. Hydrogen Phthalocyanine	4.85 "

It is contemplated that a further verification of the results in air atmosphere should be repeated particularly for 2 or 3 crystals so as to obtain concurrent results and to establish the true characteristics of these typical crystals in vacuum and other gaseous atmospheres and to establish the effect of the adsorption of gases on them. The crystals chosen for experimentation are magnesium phthalocyanine and anthracene.

II. Determination of Ionization Energies in Vacuum (up to 10-6mms of mercury)

The experimental set up consists of the same glass cross-chamber, the four limbs of which are fitted with plates carrying the necessary fittings held vacuum tight by suitable o-rings.

The pumping system consists of a two inch air-cooled oil diffusion pump (T.M vacuum products) working in conjunction with a mechanical pump (welch).

A coaxial forline trap (veeco) and other vacuum traps are connected in the line to minimize contamination of the experimental chamber with evaporated oil.

Two thermocouple gauges, one on the fore line and the other on the high-vacuum side, combined with discharge and ionization gauges measure the pressure inside the system. A pressure up to 10^{-6} mms of mercury could be attained even without the use of liquid nitrogen.

Based on the same technique of measurement, ionization energies of magnesium phthalocyanine and anthracene were determined in a vacuum up to 10^{-6} torr.

The experiment works satisfactorily and promises results of higher accuracy and dependability in a more perfected vacuum system going down to 10^{-11} mms of mercury, which experimental set up is in progress now.

Results

Substance	Ionization Energy in Vacuum (10^{-6} torr)
Magnesium Phthalocyanine	5.20 ev
Anthracene	4.86 ev

III. Determination of Ionization Energies in Ultra High Vacuum (10^{-11} torr)

Work is in progress side by side in setting up a perfect ultra high vacuum system, experiments in which would eliminate the possibility of even the least adsorption effect of any kind on the surface of the ultra pure experimental crystal under study. The results obtained no doubt will then show the true characteristics of the semiconducting crystal surface in vacuum.

The experimental layout consists of -

1) The Experimental Chamber

The central glass cross-tube chamber (specially fabricated at the university of Alabama in Huntsville) has the u-v inlet supersil window and the high voltage terminals with covar seals fused onto the proper limbs of the chamber. The condenser plates made of steel are fitted vertically at the centre of the cross tube and attached to the holders making contact with the high voltage terminals. The third limb connected to a glass-to-metal flange has provisions to insert and remove at will the quartz fibre carrying the experimental crystal. A side tube in the chamber leads to the pumping system and to a gas inlet system.

The chamber and connections are entirely of pyrex and devoid of all non-metal o-rings, thus facilitating the chamber to be heated in vacuum to $200\text{-}400^{o}{}_{C}$ in an oven so that outgassing from exposed surfaces may be eliminated fully and the crystal also presents initially a perfectly clean surface for experimentation.

2) The Pumping Unit

It consists of a mercury vapour diffusion pump (Lab Glass Co.) working in conjunction with the welch mechanical pump. Proper foreline traps and other traps are inserted in the line to eliminate backstreaming. With liquid nitrogen in the cold trap attached to the diffusion pump, the pressure in the system can be brought nearly to $10\text{-}11_{mms}$ of mercury.

The measuring gauge unit consists of proper manostats (Lab Glass), vacuum gauge traps, thermocouple and ionization gauges.

3) Gas inlet-System

Provision is also made for connecting the chamber to a gas inlet system which consists of compressed gas tubes (mathesons) like oxygen, hydrogen, nitrogen, carbondioxide, inert gases, etc., each provided with proper regulators and flow control values, and a thermocouple-discharge gauge system to measure the pressure of the incoming gas supply. An additional ion-pump is inserted in the system to exhaust, whenever necessary, the gas let in to the experimental chamber.

<u>Proposed Study</u>

The next step in the progress of the work is to determine the ionization energies of two typical cyrstals (magnesium phthalocyanine and anthracene) in ultra high vacuum and in different gaseous atmospheres having a pressure $10^{-3}{}_{mms}$. of mercury.

As indicated in the previous annual report, it is also proposed to study the effect of various encumbent gaseous pressures up to $10\text{-}3_{mms}$, and also the effect of partial pressure atmospheres of varying proportion on the surface ionization energies of the crystals under study.

Now that the experimental layout and the vacuum system is almost completed and in working order, and the experimental problems more or less under control, it is hoped that the progress of the work will be more satisfactory.

Comments

a) The main source of error in the experiment could be to ascertain for each wave length the balancing voltage when no more electrons are liberated from it. The only way to make sure of the fact was to wait a considerable period of not less than 30 minutes with each wave length or radiation to see that the crystal made no further motion after it was finally brought to the reference position on the microscope scale. Even with this extreme precaution, one cannot be too sure, as the liberation of a few electrons of the order of 10 or less may not even be indicated by any movement of the crystal at all for the quality of the fibre used.

b) In vacuum, one main difficulty in making measurements is that the crystal will be in state of slight perpetual vibration on account of the lack of damping in its environment. Still, with extreme precaution, and within error of perception, the crystal could be brought back to the exact reference position.

c) Again to avoid electrical breakdown, the experiment had to be done at comparactively lower voltages in vacuum.

d) To avoid electrons being liberated from the metallic capacitor plates by the impingement of the high energy radiation on them, and thus obscuring the true onset of photoionization of the crystal surface, the plates were given a thin insulation coating, excepting for the electrical contact points, by dipping them in a solution of paraffin dissolved in n-Hexane.

It might still be questionable whether the method can be believed to give cent percent accurate information on the absolute values of work function of the crystals under study, but it no doubt gives a highly reliable comparative study of the relative changes in surface potential of the different semiconductors in various ambient atmospheres.

Moreover, the simplicity of the method and its technique of measurement make it superior to most other methods in extending the surface studies of semiconductors under various atmospheres and partial pressure atmospheres.

Discussion

The true work function of a metal has been defined as the minimum amount of energy required to remove an electron from the surface of the metal at $0^{o}K$, and is the difference in energy of an electron at the Fermi-level just inside the surface and at rest just outside the image potential barrier in vacuum. Photoelectric threshold locates the electronic energy levels of the semiconductor surface with respect to the fermi-level. This threshold is the lowest photo - energy able to excite electrons from filled levels over the surface barrier.

In view of the Summerfold electron theory, it can be said that gases affect the photo-electric properities of a surface either through a change in the magnitude or shape of the surface potential barrier (Wa) or by a change in the potential (μ^{W}) of the electron gas within the metal. On this theory, the photo-electric threshold of a surface is given by $h\nu_0 = e\phi = wa - \mu^{W}$. The term $h\nu$ is equal to the minimum kinetic energy of the electrons in the metal. Thus, in a metal, a layer of positive ions adsorbed on the surface, would lower the work function and a layer of negative ions would increase the work function.

On the other hand, gases adsorbed throughout the body of the metal may produce an expansion of the metal crystal lattice and this might give a smaller wa. Since μ^{W} depends on the number of free electrons per unit volume, it might be altered by the presence of adsorbed gases within the body of the metal.

Photo electric emission from semiconductors is accepted to be volume effect. It has been found from work on cesiumcoated silicon surfaces(1) that p-type samples should exhibit a high photoelectric quantum efficiency than n-type samples.

Bardeen(2) has made the simple assumption that there are discrete energy states at the surface of a semiconductor, located either in the forbidden energy gap or isolated in the oxide at the surface that are capable of trapping charge or serving as recombination sites or both. If these levels are partially filled a double layer will form at the surface. With the relatively low density of free charge in a semiconductor, external electric fields can penetrate into the material for substantial distances before being shielded out. This shielding charge cloud is the surface space charge region. Depending on the sign and magnitude of the external fields, it can consist of holes or electrons. It has been pointed out that the total charge on the surface space charge region increases exponentially with surface potential.

It must also be pointed out that photoelectric emission from a semiconductor in general can arise from electrons in the valence band, in the conduction band and from surface states: Grobeli and Allen[3] have discussed the case of silicon surface emission. According to them, emission from surface states should either increase as the surface is made more n-type and decrease as it is made more p-type, or else remain constant in both cases, depending upon the presence or absence of surface states near the Fermi level at the surface. They discuss that if the electron concentration in the conduction band reaches sufficiently high values within an escape depth of the surface, emission from the conduction band should become observable. This emission would have a photoelectric threshold equal to the work function and would increase as the donor concentration increased. It is found that in the case of silicon, there is a low energy "tail" which begins to increase appreciably in n-type samples. Such samples have space charge depth of several hundreds of angstroms and the fermi level is still over o.lev below the conduction band in the bulk, and therefore the electron concentration would not reach appreciable values close enough to the surface to permit measurable emission from the filled conduction band states. The yield in the low energy tail for n-type samples in interpreted as arising from surface states in which the electron population is increasing as the sample becomes more n-type.

On the basis of these preliminary discussions, it is to be seen whether in the present investigations, the results obtained with the organic semiconductors under study in an electro-positive gas atmosphere like hydrogen or in an electro-negative gas like oxygen will give additional proof to the validity of the theories evolved[4,5,6], or, if the results are in contradiction, how it could be accounted for, and a more valid theory of the structure of the surface states and process of charge transfer could be established.

References

1) Scheer, J. J. Philips Res. Reports 15, 584 (1960)

2) Bardeen, J. Phys. Rev. 71, 717 (1945)

3) Gobeli and Allens. Phys. Rev. Vol. 127, 157-158 (1962)

4) Penney, G.W& Hummert G.T J. Appl. Phys. Vol.41, 572-577 (1969)

5) Symons, M.C.R. and Sharp, J.H. Nature Vol. 224, 1296-1297 (1969)

6) Vikram L. Dalal J. Appl. Phys. Vol. 42, 2280-2284 (1971)

Student Assistants

Mr. Melvin Jackson (Junior in Physics-Mathematics Major) and Mr. Charles Carter (a Sophomore) have been working with the project during the year. Mr. Jackson has been with the project for two years and two summers and has been able to train himself well in handling research work both in its technical aspects and in taking observations and interpreting them.

Mr. David Baldwin, a Math- physics junior has also been working with the project for a short period in June after which he has entered the Pennsylvania University on a work-study research programme for the summer.

Technical Assistance

On account of the lack of a machine shop and facilities for technical work in the college, part of the fabrication work in setting up the experimental layout was done in the University of Alabama Research Institute in Huntsville and the rest in a machine shop in the city itself.

EXPENDITURE

1.	Equipment.	...	$ 1500.00
2.	Salary:		
	Student Assistants.	....	$ 2550.00
	Principal Investigator	...	$ 4950.00
	Technical Assistance (yet to be paid)	...	$ 500.00
3.	Books and journals	...	$ 200.00
4.	Travel	...	$ 400.00
5.	Office supplies, Telephone etc.	....	$ 475.00